

## 4. Phenolic Resins

### 4.1. Introduction

**History.** The first synthetic resins and plastics were produced by polycondensation of phenol with aldehydes. In 1872 VON BAYER first reported the reaction between phenol and aldehydes. The resins formed were, however, not of industrial and certainly not of scientific interest. The phenol resin condensation was used industrially in 1902 by BLUMER for the production of novolacs, which served as a substitute for shellac.

In 1909 BAEKELAND made the first plastics. He carried out the polycondensation of phenol and formaldehyde to form cross-linked thermosets over several steps.

Besides the production of plastics, phenolic resins were sought as a replacement for natural resins, which were then used on a large scale for oil varnishes. In 1910 oil-soluble modified phenolic resins were produced by BEHREND'S by polycondensation of phenols, formaldehyde, and rosin.

Between 1928 and 1931 phenolic resins gained increased importance through the treatment of resols with fatty oils to give air-drying varnishes. The main problem, an inadequate compatibility of phenolic resins with other varnish raw materials, was solved by using alkylphenols or by etherification of the hydroxymethyl groups of resols with monohydric alcohols.

These varnish applications and the use of phenolic resins as thermosets and electrical insulating materials were the main application areas. However, other polycondensates and, above all, polymers increasingly limited the market for phenolic resins from the mid 1930s onwards. Theoretical work on

the constitution and mechanism of formation of phenolic resins was being carried out at that time by VON EULER, HULTZSCH, MEGSON, ZIEGLER, and others, which led to the development of new application areas for phenolic resins, i.e., as adhesives, printing ink binders, waterborne paints, temperature-resistant binders, and laminated plastics.

The industrial development of phenolic resins is still continuing despite the long history. Their importance is likely to remain considerable because the raw materials can be obtained at reasonable cost from both petroleum and coal. Phenolic resins can be used as raw materials for synthetic fibers and in photoresists for the production of microchips which characterizes the continuing relevance of this group of resins [1].

**Classification.** Phenolic resins are polycondensation products of phenols and aldehydes, in particular phenol and formaldehyde. DIN 16 916 (ISO 10 082) attempts to define the relevant terms and properties.

The ring hydrogens in the *para*- and both *ortho*-positions relative to the hydroxyl group can react with formaldehyde and thus cross-link to form a three-dimensional network. If at least one of these three positions bears a substituent other than hydrogen, cross-linking is no longer possible and comparatively low molecular mass compounds are formed as the end products of the polycondensation.

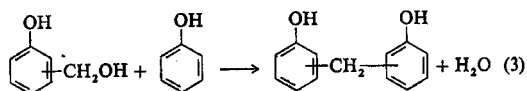
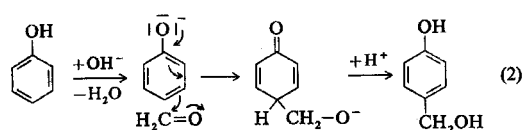
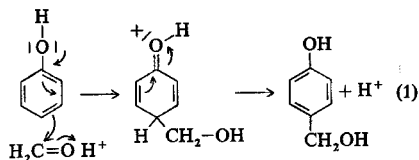
Phenolic resins are classified as novolacs and resols. In *resols* the polycondensation is base-catalyzed and has been stopped deliberately before completion. Characteristic functional groups of this class of resins are the hydroxymethyl group and the dimethylene ether bridge. Both are reactive groups. During processing the polycondensation can be restarted by heating and/or addition of catalysts i.e., resols are self-cross-linking. In the case of *novolacs* the polycondensation is brought to completion. The molecular growth of these thermoplastic synthetic resins is limited by addition of a substoichiometric amount of the aldehyde component. Novolacs are phenols that are linked by alkylidene (usually methine) bridges, without functional groups (apart from the phenolic hydroxyl groups), and cannot cure on their own. However, novolacs can be cross-linked by addition of curing agents, such as formaldehyde or hexamethylenetetramine, and give end products similar to resols.

The classification of phenolic resins into novolacs and resols is only strictly valid if phenols which are trifunctional towards formaldehyde are used as starting material, because resols from bifunctional phenols cannot cross-link by themselves. Nevertheless, the polycondensates from substituted phenols are differentiated according to their characteristic groups as *alkylphenol novolacs* (alkylidene bridge) or *alkylphenol resols* (hydroxymethyl group, dimethylene ether bridge).

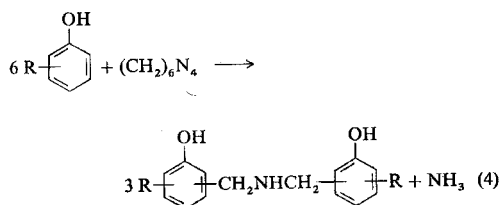
The third large group are *phenolic resins modified by natural resins*. Besides phenolic hydroxyl groups, they contain double bonds, ester links, and carboxyl groups.

**Novolacs.** The first step in phenolic resin polycondensation is always the electrophilic attack of a carbonyl compound (generally formaldehyde) on the *para*- and/or *ortho*-positions of a phenol molecule (acid catalysis, Eq. 1) or a phenolate anion (base catalysis, Eq. 2).

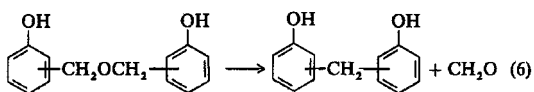
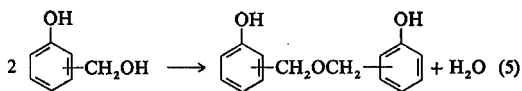
Since hydroxymethyl-substituted phenols are more reactive than phenol itself, the hydroxymethylation continues. The hydroxymethyl compounds formed are unstable in acidic medium and are rapidly converted into compounds linked by methylene bridges (Eq. 3). This reaction also occurs in both the *ortho*- and *para*-positions. In basic media hydroxymethyl groups can be stable. At higher temperatures, however, they react with the formation of methylene bridges according to Equation (3). To hinder polyalkylation by cross-linking which would make further processing more difficult or impossible, less than one mole of formaldehyde must be added per mole of phenol.



Novolacs are sometimes used as chemically unmodified synthetic resins. Their main application is based, however, on their capability to undergo cross-linking with hexamethylenetetramine. The reaction occurs at ca. 150 °C according to Equation (4) [2].



**Resols.** In a strongly acidic medium, hydroxymethyl groups are rapidly converted into methylene bridges. Therefore, the synthesis of resols can only be catalyzed by bases or salts of weak acids or bases. In analogy to the novolacs, the hydroxymethyl groups are formed in the *ortho*- or *para*-positions (Eq. 2). At temperatures above ca. 40 °C the hydroxymethyl groups can react to form dimethylene ether bridges with elimination of water, according to Equation (5). No catalyst is needed for this reaction. The dimethylene ether bridges formed are more stable in the *ortho*- than in the *para*-position. They can be converted into methylene bridges with elimination of formaldehyde (Eq. 6). The formaldehyde liberated is then available for the formation of new hydroxymethyl groups, if a suitable catalyst is present.

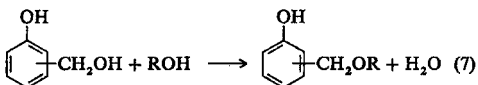


The hydroxymethyl groups of resols can also condense directly with other phenol molecules according to Equation (3). In resols therefore, three different types of formaldehyde-derived moieties occur: (1) relatively stable methylene bridges (the only type of linkage in novolacs), (2) hydroxymethyl groups, which are both capable of condensation reactions, and (3) dimethylene ether bridges.

The structure of resols depends not only on the choice of raw materials and their molar ratios, but also on the temperature of formation, concentration of raw materials, presence or absence of solvents, type of catalyst, and catalyst concentration. These parameters determine the structure to a much greater extent than in the case of novolacs.

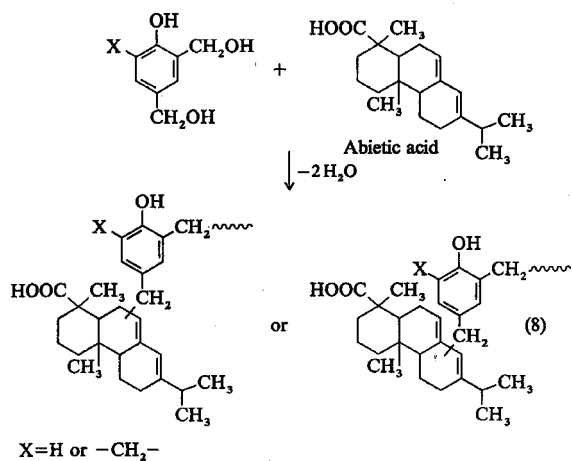
The catalyst-containing synthetic resins formed are ready to be used industrially. However, the catalyst can also be removed, either before application or during production, because no catalyst is required for the conversion of hydroxymethyl groups into dimethylene ether bridges, a rise in temperature being sufficient.

To affect compatibility (i.e., miscibility) properties the hydrophilic character of resols can be lowered by etherification of the hydroxymethyl group with alcohols according to Equation (7).



**Modified Phenolic Resins.** Rosin, a natural resin ( $\rightarrow$  Natural Resins), contains abietic acid and its double bond isomers as main components. Resols react with the unsaturated centers of these resin acids to form polycarboxylic acids with methylene bridges [3].

These condensation products from rosin and phenol – formaldehyde resin are known as albertol acids. They can be converted by esterification with polyols, or by salt formation, into higher molecular mass products which are readily soluble in nonpolar solvents but can release the solvent rapidly.



Albertol acids are also obtained by direct condensation of rosin, phenols, and formaldehyde.

Resols also undergo analogous reactions with other natural or synthetic unsaturated compounds such as fatty oils, rubbers, and polymer oils. A limited increase in the molecular mass or cross-linking can thus be achieved. Whether a particular reaction can be carried out successfully depends on the ratio of the rates of auto-condensation of the starting materials to co-condensation with the other reaction partners, but particularly on their mutual compatibility. Phenolic resins are therefore often classified as "water-soluble", "alcohol-soluble", "oil-soluble" etc.

Compatibility of resols with other components can be produced in many ways, e.g., (1) by using ring-alkylated phenols as the raw materials; (2) by etherification of the hydroxymethyl groups with alcohols; (3) by co-condensation of the resol with natural resins; or by a combination of these measures.

## 4.2. Physical Properties

Phenolic resins are yellow to brown in color, and the coloration can be very intense. Pale phenolic resins become colored immediately after production during storage or processing. The coloration is less intense only in the case of phenolic resins from *para*-alkyl-substituted phenols. Characteristic UV absorption maxima lie at 254 nm and 280 nm. The IR spectra of phenolic resins are described in [4].

Phenolic resins which are not cross-linked are commercially available as solids or solutions. For particular applications, e.g., in thermosets, the polycondensation can be driven so far that the resins are no longer soluble but can only be swelled by organic solvents. The *softening point* of solid resins can be determined by the capillary melting point according to DIN 53 244, by the ring and ball method, or similar procedures. These temperatures are not melting points in the thermodynamic sense. They charac-

terize a lowering of viscosity caused by a rise in temperature, as a result of which previously crushed resin particles can be observed to coalesce or another change in form occurs.

The *miscibility* with solvents, usually described as "solubility," depends on the structure of the resin ranging from solubility in water to that in naphtha. Resins often have limited miscibility with certain solvents.

The *viscosity* of phenolic resins or their solutions is measured at high concentrations, e.g., in 30–80% solution. Estimation of the degree of condensation from the viscosity is only possible for the same type of resin, because the molecular structure, in particular the presence of hydroxymethyl groups and dimethylene ether bridges, has a great effect on the viscosity. Usually, the results obtained do not depend on the type of viscometer used. Soluble phenolic resins have a broad *molecular mass distribution*: determination (usually by gel permeation chromatography) gives values of more than 50 000 depending on the type of phenol monomer.

Cross-linked phenolic resins are hard substances which only have a small fracture strain and cannot be melted. Decomposition reactions begin at 120–250 °C, depending on the molecular structure. There are, however, also types of phenolic resin (phenolic ether resins) which are stable for some time up to 300 °C.

Phenolic resins can be plasticized. Their compatibility with plasticizers can be adjusted by introduction of hydrophilic or hydrophobic groups.

### 4.4.1. Novolacs

In the formation of novolacs, substitution and condensation reactions occur simultaneously. In large reaction vessels formaldehyde is metered to a phenol–catalyst mixture and the rate of addition is controlled depending on the heat evolved for safety reasons. When using smaller vessels, even under laboratory conditions, care must be taken because of the exothermic reaction.

Under industrial conditions, analytical control of the course of the reaction is not necessary, because the degree of polycondensation and molecular structure of the resin are determined by the reaction conditions and the concentration of the starting materials. A temperature–time program is usually used.

**Example [5]:** 1880 parts of phenol are melted in a reaction vessel to which 50 parts of oxalic acid are added and heated to 100 °C. 1560 parts of an aqueous 30% formaldehyde solution are then gradually metered in over ca. 2 h. The reaction mixture is held at 98 °C for 5 h and the volatile parts are then distilled off under reduced pressure, until a residue temperature of 160 °C is attained at a pressure of 2.0 kPa. 1968 parts of a novolac with a softening point of 124 °C remain in the vessel.

### 4.4.2. Resols

**Resols from Trifunctional Phenols.** The production of resols differs from that of novolacs in that the reactions between phenol and formaldehyde are not allowed to go to completion but are stopped at the stage where auto-cross-linking resols are still liquid or soluble. The continuation of the condensation reactions beyond the resol stage (*A-stage*) leads to resins which are no longer soluble but can only be swelled and which are known as *resitols* (*B-stage*). The final cross-linking to form *resites* (*C-stage*) gives completely cross-linked plastics.

In resol production, the concentration of formaldehyde and the degree of condensation must be controlled during the reaction. The degree of condensation is controlled by measurement of the viscosity, if necessary, after dilution with solvents. Other possibilities include the determination of solubility, melting point, and B-time (see section 4.6). The reaction temperatures for the production of resols are between room temperature and ca. 100 °C. The molar ratio of phenol to formaldehyde can vary widely. The upper limit is determined by the functionality of the phenol towards formaldehyde (i.e., a molar formaldehyde–phenol ratio of 3:0). Resols are also formed, however, if an excess of phenol is used. In this case a major portion of the phenol does not react.

The reaction is controlled by the type and quantity of catalyst used and the temperature. High alkali concentrations (up to 1 mol per phenolic hydroxyl group) in combination with low temperatures promote the formation of hydroxymethyl groups and stabilize them. Low catalyst concentrations and high temperatures particularly promote the condensation reactions.

The catalyst can remain in the resin and—in the case of alkali hydroxides—render it water-soluble. These catalyst-containing resols can be used industrially. The catalysts can also be neutralized and, if necessary, removed by washing out or filtration. The resols thus lose their water-solubility partially or completely and must then be employed in polar organic solvents.

The heat of formation of hydroxymethyl groups is only  $-20.3$  kJ/mol, as compared with  $-98.7$  kJ/mol for the formation of methylene bridges [5]. Thus, the heat of formation of resols is theoretically lower than that of novolacs. However, hydroxymethyl groups are only stable at low temperatures and can be converted into methylene bridges at higher temperatures. Therefore, in the production of resols a great quantity of heat is evolved if the reaction gets out of control. As a result of the high formaldehyde–phenol ratio, resol production also has high safety requirements.

To *etherify* the hydroxymethyl groups, a solution of the resol is heated in, for example, butanol. The water formed is distilled off azeotropically with the organic solvent as entrainer which is recycled to the reactor. Condensation reactions between the hydroxymethyl groups to form ether bridges occur simultaneously. The reaction is controlled by measurement of the viscosity and the solubility. Etherification of alkyd- and oil-modified phenolic resins should be carried out in the presence of a plasticizer, because the compatibility between the reaction components is thus established more quickly. The distillative removal of solvents or water may be necessary during the various reaction stages or as a final step. During the distillation the condensation reactions continue. Distillation must therefore be carried out under mild conditions.

**Example** [5]. *Condensation:* 846 g (9 mol) phenol and 1600 g formaldehyde solution (30%, 16 mol) are mixed at  $20^\circ\text{C}$  and the pH adjusted to 9.5–10 by addition of concentrated aqueous sodium hydroxide solution with stirring (ca. 110 mL 38% sodium hydroxide). The mixture is heated to  $60^\circ\text{C}$  and kept for 4 h at this temperature. The decrease in formaldehyde concentration is monitored by titration with hydroxylamine hydrochloride. At the end of the reaction only ca. 1% formaldehyde is present. The mixture is cooled, and carefully neutralized almost completely with ca. 5% hydrochloric acid with stirring. The reaction solution must not become acidic and should have a pH of ca. 7.2–7.5. Water and excess phenol are subsequently distilled off in vacuum, such that the inner temperature may reach  $60^\circ\text{C}$  at maximum (at 1.5 kPa). 1360 g of viscous resin is obtained as residue.

*Etherification:* 1360 g butanol and 125 g toluene are added to the residue and the mixture is stirred at  $40^\circ\text{C}$  until the components have completely dissolved. After cooling, precipitated sodium chloride is filtered off. 900 g butanol are then added to the filtrate and the pH is adjusted to 6 with a concentrated solution of phosphoric acid in ethanol with vigorous stirring. The reaction mixture is then heated to boiling with stirring in a three-necked flask fitted with a Dean–Stark head which is filled with a 1:1 butanol–toluene mixture. In the Dean–Stark head, the water which has been distilled off is separated and the solvent is recycled into the reaction vessel. After ca. 72 mL water have been distilled off, a sample of the reaction solution can be diluted at  $20^\circ\text{C}$  with 4 parts of xylene or 1.4 parts of petroleum ether without the resulting solution becoming cloudy (before the etherification a sample could only be diluted by 0.7 or 0.4 parts, respectively). The solution is concentrated to 2620 g in vacuum and traces of salt are filtered at  $20^\circ\text{C}$  after 48 h.



## 4.7. Uses

### 4.7.1. Novolacs

#### 4.7.1.1. Cross-Linked Novolacs

For cross-linking, novolacs are processed together with *curing agents*, mainly hexamethylenetetramine. Cross-linking occurs at a sufficient rate at 140 – 160 °C and can be carried out within a few minutes, particularly if a part of the polycondensation reaction has already taken place.

Novolacs are sometimes cross-linked with *resols*. This reaction gives resites with high hardness, high stability, but a very low fracture strain.

The deflection under load is tested according to Martens. According to DIN 53 458 and DIN 53 462, the fatigue strength at elevated temperatures is determined from properties such as the weight loss after storage in air or under an inert gas. Cross-linked phenolic resins are much less inflammable than thermoplastics. Phenolic resins can be rendered virtually nonflammable by the addition of usual plastics additives such as phosphates, borates, halo compounds, red phosphorus, phosphoric acid esters, or antimony trichloride. This is particularly important if other inflammable substances are used as fillers or for reinforcement.

**Thermosets.** Phenolic resin molding materials are produced with heated rollers or extruders. Treatment of a mixture of novolac, hexamethylenetetramine, fillers, and additives leads to an intermediate, the actual molding material. The polycondensation is driven so far that the molding material in the final molding step can still flow, but so that the final cross-linking occurs very quickly. Phenolic resin thermosets are standardized according to DIN 7708, part 2. The application properties of the final products depend very much on the choice of filler material. The processing properties, in contrast, are affected primarily by the novolacs used. Especially important processing properties are good flow characteristics and rapid curing. Molding technology which predominated until the end of the 1960s has in the meantime been substituted by transfer molding and injection molding, particularly in the mass production of less complicated preforms. Thus the expression “thermosetting molding materials” has come into common use.

*Grinding Wheels.* In the production of phenolic resin-bound grinding wheels, the grinding material (usually corundum of various granularities) is impregnated with a liquid phenol resol and mixed with a ground, pulverized mixture of phenol novolac and hexamethylenetetramine. The binder cures to a three-dimensional cross-linked resite under a carefully controlled temperature and pressure program. No defects may occur in this process because grinding wheels are exposed to high thermal and mechanical stresses (DIN 69 100, DIN 69 111).

*Friction Linings.* Brake linings and clutch facings are made of reinforced phenolic resinbound thermosets. Novolac–hexamethylenetetramine mixtures can also be used here as binders. For better heat conduction, copper wire or copper gauze is often incorporated. Novolacs modified with alkylphenols or cashew oil are used to adjust hardness and lubricating properties, particularly in brake linings.

**Reinforcing Resin for Rubber.** The hardness of rubber is increased by the incorporation of novolac–hexamethylenetetramine mixtures. This hardness can be so great as to enable fabrication of solid, tough molded articles, for example for bodywork parts. Often, however, as in car tire mixtures, only slight improvement of the rubber hardness is aimed at. The reinforcing effect is thought to be caused by strong intermolecular interactions between the cured, duroplastic phenolic resin and the rubber-elastic vulcanized product. Both types of macromolecule are not bonded by covalent bonds.

#### 4.7.1.2. Novolacs without Cross-Linking

The use of novolacs which are not cross-linked is less important and is based particularly on their solubility and compatibility properties. As polyalkylidenephenols they have strong inter- and intramolecular interactions and can be adapted to the most varying requirements by alkyl substitution.

*Varnishes.* The use of non-cross-linked novolacs in varnishes is the oldest application of phenolic resins. Because of their high susceptibility towards oxidation and coloration, particularly in the case of unsubstituted phenol novolacs, this application area has hardly developed further. Non-cross-linked novolacs are now only important in specialist areas such as model lacquers and bituminous paints.

*Printing Technology.* Novolacs are often added to aniline printing inks because of their high affinity for these dyes. Because aniline printing inks are often used for printing on food packaging materials, the novolacs must be phenol-free. Novolacs are also used in the formulation of ballpoint pastes.

Novolacs are applied together with diazo compounds to zinc or aluminum plates in a thin layer for production of positive offset printing plates. Similar systems are used as photoresists for the photolithographic production of integrated circuits.

*Raw Materials for Epoxy Resins.* The reaction of epichlorohydrin with novolacs (instead of bisphenol A) leads to polyfunctional epoxy resins (→ Epoxy Resins). Their curing products are characterized by their particularly high usage temperatures.

*Alkylphenol novolacs*, particularly those based on 4-hydroxybiphenyl, 4-isooctylphenol, and formaldehyde are used for the production of copying paper.

*Tackifiers for Rubber.* Nonvulcanized rubber mixtures are often not tacky enough to adhere to each other. This is a considerable disadvantage in the production of laminated rubber articles, e.g., car tires. Tackifiers are used in rubber technology to improve this. Besides mineral oils and natural and synthetic resins, alkylphenol novolacs are particularly effective and when used with other tackifiers have a synergistic effect. In

addition to alkylphenol–formaldehyde novolacs, *para*-alkylphenols–acetaldehyde resins, and *para*-alkylphenols–acetylene resins are often used as tackifiers.

*Crude Oil Separators.* Ethoxylation (i.e., reaction with ethylene oxide) of alkylphenol novolacs gives water-soluble, surface-active substances. If the degree of ethoxylation is suitably adjusted, they have de-emulsifying properties. Addition of small quantities to the crude oil that is extracted as an oil–saltwater emulsion effects a faster separation into an oil and an aqueous phase.

## 4.7.2. Resols

### 4.7.2.1. Water-Soluble Resols

Condensation products of phenol and formaldehyde, which are present as water-soluble phenolates, are used mainly as adhesives for wood or wood chips, as binders for organic and inorganic fibers and for granular material such as corundum or sand. Curing is performed thermally at 100–180 °C and, if possible, under pressure. If curing is carried out under atmospheric pressure, the cross-linking process must be carefully controlled and performed slowly to avoid the formation of bubbles or cavities.

The waste-gas from the thermal curing process contains phenol, formaldehyde, and sometimes solvent vapors. When legally stipulated limiting values are exceeded, the waste-gases must be incinerated.

Cross-linked phenolic resins have a low flammability. They can be rendered virtually nonflammable by additives. In the event of fire the flue gases are relatively nontoxic and, compared to the flue gases from other burning plastics, are relatively transparent. This makes them particularly suitable for the interiors of vehicles, places of assembly etc.

*Chipboard Adhesives.* The greatest quantity of aqueous, alkaline resol solutions are used in the production of wooden chipboard. Chipboard bound by phenolic resin is moisture-resistant in contrast to that bound by urea resins, and is therefore suitable for the production of exterior walls in buildings and related uses.

*Construction Adhesives.* Resorcinol–formaldehyde resins are used as wood glues. Resorcinol is treated with a substoichiometric amount of formaldehyde in an alkaline medium and the stable solution is treated with more formaldehyde (usually in the form of paraformaldehyde) immediately before use. The polycondensation with resorcinol, which is very fast at, and even below, room temperature is thus restarted. The resorcinol–formaldehyde resin cross-links three-dimensionally. Glueings containing resorcinol resins have high mechanical stability and are highly water-resistant.

*Binding Agents for Molding Sand.* Phenol resols or novolac–hexamethylenetetramine mixtures which can be sufficiently diluted with water, are used as binders for casting molds, which consist mainly of sand. Mixtures of both resins are sometimes used for full molds. For hollow and thin-walled molds (Croning process), alcoholic solutions of novolac–hexamethylenetetramine adducts are used. To achieve special properties or to

make the process cheaper, phenolic resins are sometimes modified with furan or urea resins.

*Laminates.* High quality laminates for electrical equipment are obtained by impregnation of paper with phenolic resins and subsequent thermal cross-linking. They are used as insulation and construction materials. Unmodified resols and oil-plasticized resols are used together for impregnation. Both resins have different functions. The unmodified resins—with as low a molecular mass as possible—penetrate into the fiber and the oil-plasticized resins remain on the fiber surfaces and bind them together.

In *decorative laminates*, water-soluble, alkaline resol solutions can only be used for the production of core resins because of their dark coloration. Melamine resins are used as decorative facings.

*Fiber Bonding.* Organic or inorganic fibers or rock wool can be bonded to plates or nonwoven fabrics by impregnation with an aqueous resol solution or this can be sprayed on them. Curing is carried out continuously with heated rollers or in presses. Matting or insulating plates bound with phenolic resin have heat-insulation properties similar to thermoplastic foams, but have the advantage of being virtually nonflammable and at the same time soundproof.

*Foamed Plastics.* Water-soluble resols can be used for the production of foamed plastics after neutralization and, if required, removal of the basic catalyst. For foaming, the addition of surfactants and the use of blowing agents (i.e., low-boiling or halogenated hydrocarbons) is necessary. Phenolic resin foams have the advantage of low flammability. However, the corrosive effect of the strong acids used as hardeners limits their general use.

*Abrasives.* To produce abrasives such as sandpaper, abrasive cloth, or flexible sanding disks on vulcanized fiber, abrasive grains are applied to a moving backing cloth on one side. These grains are fixed together and to the surface of the backing cloth with a binder. For heat-resistant abrasives, phenol resols are preferably used as binders.

Since the carrier material (usually cellulose) is sensitive to high temperatures, a prolonged application of temperatures  $>130^{\circ}\text{C}$  must be avoided. Therefore, cross-linking of the phenol resol to resite takes a long time. Phenolic resins that are suitable for the production of abrasives must therefore be very reactive, to limit the curing time to a few hours. This naturally limits their storage life. The cross-linking reactions are carried out under atmospheric pressure in sloping dryers and the carrier materials, coated with phenolic resin, and abrasive grains are introduced in sloping loops through channels, whose temperature and humidity must be carefully controlled.